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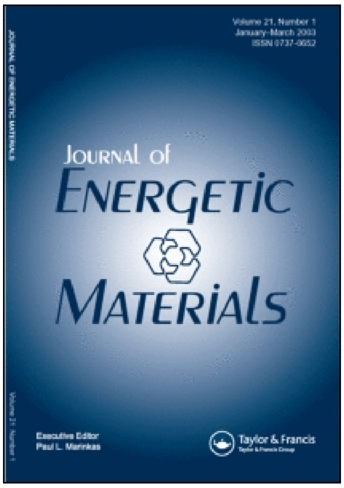

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Synthesis and characterization of 2,4,6-tris (3', 5'-diamino-2',4',6'-trinitrophenylamino)-1,3,5-triazine (PL-1): A new thermally stable insensitive high explosive

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SYNTHESIS AND CHARACTERIZATION OF 2,4,6-TRIS (3', 5'- DIAMINO-2',4',6'-TRINITROPHENYLAMINO)-1,3,5-TRIAZINE (PL-1) : A NEW THERMALLY STABLE INSENSITIVE HIGH EXPLOSIVE.

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ABSTRACT

2,4,6- tris (3',5'- diamino-2',4',6'-trinitrophenylamino)-1,3,5-triazine (PL-1), has been synthesized in 29-31% overall yield from cyanuric chloride and 3,5-dichloroaniline following condensation, nitration and amination reactions. The structure of the compound has been assigned on the basis of spectral data (IR, ^1H - NMR and Mass) and elemental analysis. Some of the physico-chemical and explosive properties including thermal behaviour of the compound are also reported.

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INTRODUCTION

From 1960 onwards, a number of research groups including our own have been involved in the study of nitroaromatic substituted heterocyclic compounds for use as heat resistant explosive[1-4]. It is believed that the itroduction of heterocyclic groups, and the alternation of nitro and amino groups, can result in an increase of density and heat resistance and at the same time, a decrease of impact sensitivity[5,6].

During the course of our study on, 2,4,6–tris(2-nitro-benzo-difuroxanyl)-1,3,5-triazine[7], 2,4,6-tris(3',5'-diamino-2',4',6'-trinitrophenylamino)-1,3,5-triazine (PL-1) was prepared. As expected from the high nitrogen content and the presence of amino groups, it showed good insensitivity and good thermal stability. We report here details of synthesis, characterization and to a lesser extent the explosive and thermal behaviour of the compound.

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EXPERIMENTAL

All melting points were determined at 2°C/min and are uncorrected. IR Spectra were recorded with Perkin-Elmer Infrared Spectrophotometer on KBr pellets. ^{1}H -NMR spectra were determined on Bruker 90 MHz, model WG-90 with a pulsed Fourier Transform system, spectra were recorded at ambient temperature (near 30°C), chemical shifts are reported in δ units (parts per million ,ppm) values using tetramethylsilane (TMS) as internal standard. Mass Spectrum was recorded on JEOL-DS-Spectrometer. Elemental analysis was performed on Elemental Analyzer EA-1101. Thus, purity was confirmed by chromatography (silica gel-'G'; acetone-dichloromethane; 4:1 as solvent system) .

Differential thermal analysis studies were performed on the micro-DTA apparatus fabricated in our Laboratory by heating 10 mg of the sample at a heating rate of 5°C/min in presence of static air. Deflagration temperature was determined by heating 0.02 g of sample in a glass tube in Wood's metal bath at a rate of 5°C/min and the temperature at which it got ignited was recorded[8]. Impact sensitivity measurements were carried out on impact machine uing 2 kg wt. dropped from a height as varied according to Bruceton "Staircase" method[9] and friction sensitivity measurements were carried out by Julius Peter's apparatus by following standard methods[9].

Materials : Cyanuric chloride was obtained commercially from E-Merk (India) Ltd. 3,5-dichloroaniline was a product of Lancaster make. Fuming nitric acid and oleum were obtained from High Explosive Factory, Pune and were used as such.

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Synthesis : The synthesis of 2,4,6–tris(3,5-diamino-2,4,6-trinitrophenylamino)-1,3,5-triazine involves three steps.

1. Synthesis of 2,4,6-tris(3',5'-dichlorophenylamino)-1,3,5- triazine
2. Synthesis of 2,4,6-tris(3',5'-dichloro-2',4',6'-trinitrophenylamino)-1,3,5- triazine
3. Synthesis of 2,4,6-tris(3',5 -diamino-2',4',6'-trinitrophenylamino)-1,3,5-triazine

2,4,6-tris(3,5-dichlorophenylamino)-1,3,5- triazine[10] (1)

Cyanuric chloride (1.84 g; 0.01 mole) and 3,5-dichloroaniline (4.86 g; 0.03 mole) were taken in a 250 ml capacity of three-necked flask. Dimethylformamide, DMF (30 ml) was run into it. The mixture was heated at 85 to 90°C with constant stirring for 5 hrs. It was then allowed to chill followed by addition of crushed ice into the mixture. The precipitate thus formed was collected by filtration and washed thoroughly with water and finally dried, giving 5.2 g (90%) of the product. The compound did not melt below 300 °C, but changes colour at 330°C.

IR(KBr)cm^{-1}: 3398(-NH str), 3088(Ar-H), 1620(C=N str.), 1574(-NH bend),
1114(arom. in- plane bend and C-N str), 920 (Ar- Cl),
830,802 (arom. Out-of –plane & -NH wagg.)

^{1}H-NMR (DMSO-d_6/TMS) δ ppm: 9.77(s,3H,NH), 7.80(s,6H,phenyl),
7.25(s,3H, phenyl)

Analysis Calcd. For $C_{21}H_{12}N_6Cl_6$: C,44.92; H, 2.14; N, 14.97; Cl,37.97
Found: C,44.58; H, 2.39; N, 14.58; Cl,37.60

2,4,6-tris (3',5'-dichloro-2',4',6'-trinitrophenylamino)-1,3,5-triazine[10] (2)

Oleum (55 ml, 0.603 mole) was taken in a three neck round bottom flask.

Fuming nitric acid (11.4 ml, 0.266 mole) was added dropwise under stirring maintaining the temperature 10 to 15°C. After complete addition of nitric acid, condensed product, 1 (5.61 g, 0.01 mole) was added portionwise to the mixture with stirring. The resulting mixture was stirred for an additional half an hour and then refluxed for one hour at 85° - 90°C. The mixture was then allowed to cool and then poured into the crushed ice. The precipitated product was then collected by filtration, subsequently washed with water till free from acid and finally dried to yield 3.3 g (65-70%), m.p. 270 °C (decompn), DTA (Exo) 290°C.

IR(KBr) cm^{-1} : 3374 (-NH str), 1556 (-NO_2 -asym), 1490 (-NH bend), 1400 (C-N str), 1346 (-NO_2 sym), 1094 (arom.skeletal), 940 (Ar-Cl)

Analysis Calcd. For $C_{21}H_3N_{15}O_{18}Cl_6$: C, 26.08; H, 0.31; N, 21.73, Cl, 22.04

Found : C, 26.50; H, 0.29; N, 21.23; Cl, 21.70

2,4,6-tris(3',5'-diamino-2',4',6'-trinitrophenylamino)-1,3,5-triazine (PL-1)

To 100 ml acetone in a 250 ml three necked flask the intermediate nitro compound, 2 (2 g, 0.002 mole) was added portionwise with constant stirring at room temperature until the solution became homogenous. The temperature of the solution was then raised to 50 ± 5°C and ammonia gas was passed for 12-13 hrs till complete precipitation occurred. The reaction mixture was allowed to cool and the product was separated by filtration, washed with acetone and finally dried to yield 0.8 g (50%) m.p. 336 °C (decompn).

IR(KBr) cm^{-1} : 3318, 3218 (-NH asym & sym), 1608 (-NH bend), 1556 (-NO_2 asym), 1446 (arom. Skeletal) 1224 (-NO_2 sym), 1172 (N →O str), 730 (-NH wagg.)

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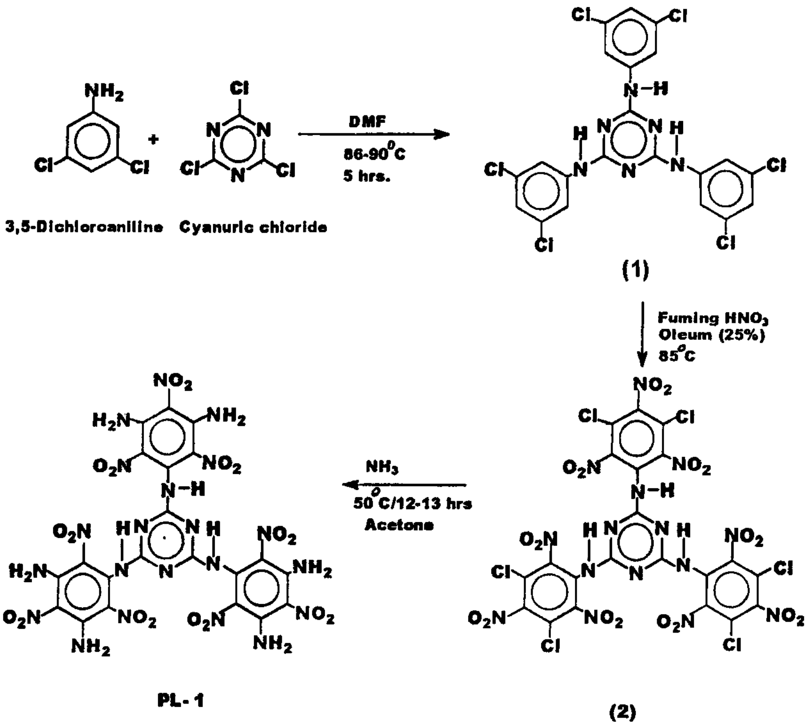
Analysis Calcd. For $C_{21}H_{15}N_{21}O_{18}$: C, 29.68; H, 1.76; N, 34.60

Found : C, 29.35; H, 2.10; N, 34.63

RESULTS AND DISCUSSION

2,4,6-tris(3',5'-diamino-2',4',6'-trinitrophenylamino)-1,3,5-triazine was prepared in 50% yield by amination of 2,4,6-tris (3',5'-dichloro-2',4',6'-trinitrophenylamino)-1,3,5-triazine which in turn was prepared from condensation of cyanuric chloride and 3,5-dichloroaniline followed by nitration with mixed acid (Scheme-1).

Scheme -1



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PL-1 is a yellow solid and difficult to dissolve in organic solvents. The compound was prepared in good yield and a substantial improvement of yield has been achieved by the duration of continuous flow of ammonia gas into the reaction mixture. It has been characterized satisfactorily by spectral data (IR, ^{1}H- NMR & Mass) and elemental analysis results. The results of elemental composition also confirm the absence of chlorine. The electron impact (EI) mass spectrum was recorded at 70 eV. However, the molecular ion was not detected due to the high molecular weight and low volatility. Fast atom bombardment (FAB) technique appears to be more appropriate for this type of molecule, but we lack those facilities. However, the EI at 70 eV spectrum showed the prominent peaks at m/z 257, 242, 123, 91 and 81, can be assigned to the expected fragmentation species.

In search of new high energy and low sensitivity explosives, alternating amino and nitro groups were introduced into the multiphenyl groups to increase densitry and thermal stability in this compound. PL-1 has considerably low hydrogen content, high nitrogen content and good heat resistance with decomposition temperature 335°C (DTA 10°C/min), which represents the temperature somewhat below which it may be used. The compound has a density 2.02 g/cm^3 (determined by the method of the density bottle)[11], detonation velocity[12], 7861 m/s and has the oxygen balance, -59.36 %. PL-1 has promising blend of insensitivity to friction (≅ 36 kg) and impact (height for 50% explosion) 170 cm. As compared to a moderately powerful heat resistant explosive, 2,6-bis (picrylamino)-3,5-dinitropyridine (PYX), PL-1 is superior in

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properties and the overall comprehensive properties of PL-1 are equivalent to that of Triaminotrinitrobenzene (TATB), the thermally stable insensitive molecule(Table-1).

Further, the compound was examined on a Differential Thermal Analysis (DTA) instrument for thermal decomposition studies at different heating rates with an interval of 5°C/min. The data (Table-2) show that it exhibits exothermic peaks increasing at different heating rates indicating that the compound is thermally and chemically stable. The activation energies at decomposition temperatures have been calculated by adopting the method of Ozawa[13] and Kissinger[14], and are found 47.346 Kcal/mole and 45.787 Kcal/mole respectively.

A combination of thermal stability and impact insensitivity creates a renewed interest in our further investigation on the compound.

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TABLE- 1 : SOME CHARACTERISTIC COMPARATIVE PROPERTIES OF PL-1, PYX AND TATB

Sr.No	PROPERTIES	PL-1	PYX	TATB
1	Melting point, °C	336	300(decompn)	360
2	DTA (exotherm), °C Ti	325	350	336
	Tm	335		360
3	Density, g/cc	2.02	1.75	1.94
4	Impact sensitivity, cm (height of 50% explosion)	170	67	180
5	Friction sensitivity, kg (insensitive upto)	36	36	36
7	Oxygen balance, %	-59.36	-55.39	-55.81
6	Velocity of Detonation, m/s (Calcd)	7861	7260	8000
8	Detonation Pressure (Calcd), Kbr	312	230.5	310.4

TABLE- 2: THERMAL DATA OF PL-1 AT DIFFERENT HEATING RATES

Sr. No	HR °C	Tm °C.	Tm °K	1/Tm	Tm^2	log β	ln β	Ln (β / Tm^2)
1	5	338.7	611.7	1.6347×10^{-3}	374176	0.6989	1.6094	-11.223
2	10	348.7	621.7	1.6084×10^{-3}	386510	1.0000	2.3025	-10.5623
3	15	355.1	628.1	1.592×10^{-3}	394509	1.1760	2.7080	-10.1773
4	20	360.3	633.3	1.579×10^{-3}	401068	1.3010	2.9957	-9.9061
5	25	363.5	636.5	1.571×10^{-3}	405132	1.3979	3.2188	-9.693

Methods

Activation Energy (Ea), Kcal/mole : Ozawa[13] Kissinger[14]

47.34 45.78

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Scheme -1